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(54) Title: THERMOPLASTIC ELASTOMER

(57) Abstract

The invention relates to a thermoplastic elastomer comprising a blend of a rubber and a thermoplastic resin, the rubber being at least partially cured. The invention is characterized in that the thermoplastic elastomer comprises: A) a thermoplastic resin, B) an amorphous polyolefin, selected from an amorphous α -olefin homopolymer, in which the α -olefin has 3-20 C-atoms, and an amorphous α -olefin copolymer, based on ethylene and a α -olefin having 3-20 C-atoms, and C) an at least partially cured rubber, wherein the ratio of component (B) to components (A + B) is between 15 and 75 wt.%, the component C is present between 25 and 90 wt.% (based on (A + B + C)), and wherein the amorphous polyolefin (component B) is uncured.

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THERMOPLASTIC ELASTOMER

5

The invention relates to a thermoplastic elastomer comprising a blend of a rubber and a thermoplastic resin, the rubber being at least partially cured.

10

Such a product is known from US-A-4,130,535, where a cured (or vulcanized) thermoplastic elastomer (or thermoplastic vulcanizate, TPV) is made from a polyolefin resin and an olefin rubber.

15

The at least partially cured state of the thermoplastic elastomer is obtainable by subjecting the rubber or a blend of uncured rubber and thermoplastic resin to a curing process. This process can be static or dynamic and be done by the use of known curing agents, like peroxides or phenolic resins.

20

A defect of such a thermoplastic elastomer is that the hardness of such a product, at a same amount of rubber, can hardly be lowered without sacrificing other properties. One of the possibilities to obtain a lower hardness thermoplastic elastomer is the use of styrene block copolymers, either as such or in combination with the TPV. This ingredient is however expensive and its use is therefore restricted. An alternative is the addition of extender oil for lowering the hardness, but apart from the fact that the hardness reduction is relative small, other physical properties (like tensile strength) deteriorate. This addition also results in increased fogging of the product (i.e. ingredients evaporate from the surface) as well as the sweating-out of the oil (i.e. the oil migrates to the surface of the product and gives it an oily appearance).

There is therefore a need for a thermoplastic elastomer not having these deficiencies.

The invention is characterized in that the thermoplastic elastomer comprises:

- A) a thermoplastic resin
- B) an amorphous polyolefin, selected from an amorphous α -olefin homopolymer, in which the α -olefin has 3-20 C-atoms, and an amorphous α -olefin copolymer, based on ethylene and a α -olefin having 3-20 C-atoms, and
- C) an at least partially cured rubber,

10 wherein the ratio of component B to components (A + B) is between 15 and 75 wt.%, component C is present between 25 and 90 wt.% (based on (A+B+C)), and wherein the amorphous polyolefin component B is uncured.

15 The presence of component B is essential for obtaining the effects of the present invention. This component is uncured and should remain as such during further processing.

20 The invention is specifically applicable in those cases where a high amount of rubber is desired (which also corresponds to low-hardness products).
25 In EP-A-109,375 it is indicated that a too high amount of rubber results in crumb formation; in said publication this problem is (said to be) overcome by a two-step vulcanisation, where in each step only part of the total rubber is added and vulcanized. The thermoplastic elastomers of the present invention are obtainable with a one-step process.

30 The present invention provides also thermoplastic elastomers with a hardness of less than 35 Shore A. This is the more surprising, as a publication (in Plast. Techn. Jan. 1996, page 47) indicates that a 35 Shore A thermoplastic vulcanizate is the softest grade available.

35 In the following, the essential constituents of the thermoplastic elastomer of the present invention will be dealt with.

A) Thermoplastic resin

The thermoplastic resin may be any polymer which behaves like a thermoplastic in the temperature range between 100 and 350°C; care should be taken that the processing temperature (i.e. the temperature at which the thermoplastic elastomer is prepared or used) is sufficiently lower than the decomposition temperature of the resin. Examples of such resin are thermoplastic resins like polyesters, nylons, polycarbonates, styrene/acrylonitrile copolymers as well as the preferred thermoplastic polyolefin resins. In the latter case, preference is given to polyethylene and polypropylene, as a homopolymer as well as copolymers with up to 20 wt.% of another α -olefin. The thermoplastic resin preferably has a crystallinity (measured with DSC (differential scanning calorimetry)) of at least 25%.

B. Amorphous polyolefin

The amorphous polyolefin is a homo- or copolymer of an α -olefin having a random structure, which deviates from the structures in crystalline polyolefins which are of the isotactic or syndiotactic form. In general these products have a crystallinity (measured by DSC) of less than 10%; preferably the crystallinity is below 3%.

The α -olefin in an amorphous homopolyolefin can be any α -olefin having 3-20 C-atoms; preference is given to propylene as the α -olefin; i.e. preferred as component B) is amorphous polypropylene as the amorphous homopolyolefin. Next to or instead of an amorphous homopolyolefin, component B can also be an random, or amorphous, α -olefin copolymer, based on ethylene and another higher α -olefin as comonomer. A suitable comonomer is a comonomer with 3-20 C-atoms.

To be effective in the thermoplastic elastomer of the invention, component B has to have a

number average molecular weight M_n (determined with SEC-DV (size exclusion chromatography, coupled with a differential viscosimetry)) of at least 20,000. More preferably, the M_n of component B is at least 25,000.

5 The component B has to be present in the thermoplastic elastomer in a (substantially) non-cured form. In case component B is curable, the occurrence of such effect is to be avoided. This is especially the case in which the curative for component C can also 10 cure component B (like e.g. a peroxide as curative). In such a case, and that is part of the process for preparing such a TPV, the component B is preferably to be added after the completion of the curing process of the rubber.

15

C. Cured rubber

The rubber present in the thermoplastic elastomer of the present invention may be any natural or synthetic rubber which can be cured with as such known curatives, like peroxides, phenolic resins, 20 maleimides or silicon based curatives. Suitable rubbers according to the invention are acrylrubber, butyl-rubber, halogenated rubber (like brominated and chlorinated isobutylene-isoprene rubber) (styrene-) 25 butadiene rubber, butadiene-styrene-vinylpyridine rubber, nitril rubber, natural rubber, urethane rubber, silicone rubber, polysulfide rubber, fluorcarbonyl rubber, ethylene/α-olefin (diene)rubber (EA(D)M-rubber), polyisoprene, epichlorohydrine rubber, chlorinated polyethylene, polychloroprene, chloro-sulphonated polyethylene. Preference is given to 30 ethylene/α-olefin/diene terpolymer (EADM) rubber and to butylrubber. The EADM contains as the second monomer an α-olefin, which can be propylene, butene-1, 35 pentene-1, hexene-1, octene-1 or the like or a branched isomer thereof like 4-methylpentene-1, and further styrene, α-methylstyrene and the like. Also mixtures of

α-ol firs ar applicabl . Pr f r nce is giv n to propylen and/or but n -1 as th α-olefin. Gr at r preference is given to propylene; the resulting terpolymer is a ethylene/ propylene/diene terpolymer 5 (EPDM).

The third monomer in such an EADM or EPDM can be any conventionally applied monomer in such rubber, like hexadiene 1,4, dicyclopentadiene or ethylidene norbornene. Preference is given to ethylidene 10 norbornene as third monomer.

The butylrubber, which can be an essential element of the thermoplastic elastomer of the present invention, is an amorphous copolymer of isobutylene and isoprene or an amorphous terpolymer of isobutylene, 15 isoprene and a divinyl aromatic monomer. The term "butylrubber" also comprises the halogenated form of the above mentioned co- and terpolymer. Thermoplastic elastomers based on butylrubber are disclosed in e.g. US-A-4,130,534 and EP-A-376,227.

The thermoplastic elastomer comprises 25-90 20 wt.% of rubber (component C) per 100 parts of components (A + B + C), more preferably between 40-75 wt.%.

The amount of the thermoplastic resin 25 (component A) is preferably between 5-25 wt.% per 100 parts of components (A+B+C). It has been found that such low amounts of thermoplastic resin in a thermoplastic elastomer are only attainable due to the presence of component B. In the absence thereof, the 30 products become unprocessable after curing.

The relative amount of component B towards components (A + B) is general between 15 and 75 wt.%; more preferable this is between 20 and 70 wt.%.

Components A and B can form separate 35 ingredients of the thermoplastic elastomer of the invention, but can also be constituents of a blend, prepared during a polymerization process. Such a blend,

also referred to as amorphous lastomeric oilfin polymer, is described in EP-A-475,306. Such products are made e.g. by Rexene under the trade mark Rexflex and marketed as flexible polyolefin.

5 The rubber in the thermoplastic elastomer (component C) is at least partially cured. One method for determining the degree of curing is by measuring the amount of rubber, extractable from the TPV by using boiling xylene as the extractant. Such a method can be
10 found in e.g. US-patent no. 4,311,628.

15 According to such a method, the rubber (component C) in the thermoplastic elastomer of the invention is generally cured to the extent that not more than 50%, preferably not more than 15%, and even more preferred not more than 5%, of the rubber is
15 extractable in boiling xylene.

20 The thermoplastic elastomer can contain other additives and fillers commonly used in these types of products, like carbon black, pigments, flame retardants, UV-stabilizers, UV-absorbers, processing aids, extender oils etc.

25 In case components A and B are not significantly compatible with each other, there are several ways to improve this. One possibility is the modification of component A and/or component B with the aid of functional groups which improve the compatibility of the two components A and B. This can be done for instance in the case the A-component is a
30 polar resin, like nylon, by modifying the B-component through the introduction of a polar functionality in compound B, e.g. by grafting an anhydride of amine functional group to component B.

35 Another alternative is the use of a separate ingredient, suitable for compatibilizing the components A and B. Such ingredients (or compatibilizers) are well known in the art and the skill'd man is aware of the criteria to be applied in such case.

The process for preparing the thermoplastic elastomer can be any process by which a blend of an at least partially cured rubber and a thermoplastic resin can be obtained. Preference is given to a process in which the blend is made by dynamic curing (i.e. the process of mixing and curing of the rubber and the thermoplastic resin are taking place in one process step). It is to the skilled man to avoid severe premature curing while the mixing process is not completed. Reference can be given to the above mentioned US '628 and US '535 patents. Equipment to be used in a process according to the invention can be any mixing apparatus for blending polymers. Reference can be had to batch equipment (like Banbury mixers); preference is given to continuous operating equipment, like a twin screw extruder. Care should be taken that all ingredients are well-mixed.

In the process of the present invention it can be of advantage to premix components A) and B) before the incorporation of component C). In case components B and C are both curable by the curing agent to be used for curing component C, the process for preparing the thermoplastic elastomer of the present invention should be such that component B is added after the (dynamic) vulcanisation of component C, - or components A+C, is completed.

In case a thermoplastic elastomer with a high percentage of component C is to be made, care should be had that crumb formation is avoided. If this is a potential problem, then the addition of component C should be performed before the curing process. Alternatives are to be evaluated in case a co-curing of components B and C could occur. Possibilities (non-exhaustive) are selection of another type of amorphous product B or another type of curative (like a one which only cures component C and not component B).

The products of the present invention are

useful for making a variety of articles like hoses or moldings. These articles can be made by extrusion, injection or compression moulding techniques. They are especially useful in those types of applications where the improved properties of the TPV are of excellent use, like in low-hardness applications (like the so-called soft-touch application) where the products can replace soft PVC, or where the reduced fogging and oil-swell are of interest. Examples of such applications can be speakercones, seals, tubings, medical containers and others.

The thermoplastic vulcanizates of the invention are also very suited to prepare elastic fibers. These fibers have a titer of 1-1000 tex, preferably between 2 and 500 tex and most preferred between 5 and 250 tex. (a "tex" being the weight (in grams) of 1000 mtrs of fiber (g/1000m)). The elongation at break amounts at least 100% and can be as high as 400% or even 600%. The fibers are suitable to give elastic properties to textile materials, fabrics and knittings. The fibers can also be used in combination with other fibers, like polyamide or cotton fibers. The fiber can be prepared by a melt spinning process of the thermoplastic elastomer of the present invention. The equipment suitable for such a process is known to the skilled man and comprises at least a unit containing the molten thermoplastic elastomer and a spinnerette having one or more openings to form the fibers from the molten thermoplastic elastomer. The equipment to produce the thermoplastic elastomer and the equipment to produce the fibers therefrom can be integrated in one apparatus, like in an extruder provided at its exit with a spinnerette.

The thermoplastic elastomer of the present invention has unexpectedly improved properties compared to conventional TPV's having a same content of at least partially cured rubber. It can be mentioned that

specially the blow moldability, the tension set and the foamability are improved. As a result therefore, thermoformed products are now attainable in low hardness grades, products which until now were not 5 available at all, or only available at a considerable higher cost price or with inferior physical properties.

The invention will be elucidated by the following examples and comparative experiments. They are not intended to form in any way a restriction of 10 the invention.

The physical properties, as used in the Tables, are:

	CS:	compression set, according to ISO 815
15	M:	elastic modulus, according to ISO 37
	TS:	tensile strength, according to ISO 37
	EB:	elongation at break, according to ISO 37
	ΔH:	heat of crystallisation, determined by DSC
	T _m :	melting point, determined by DSC.
20	tex:	weight (g) of 1000 metre fibre (g/1000m)
	tenacity:	according to BS 5421, part 2, 1978, and based on original fineness
	tension set:	5 cm fibre is deformed up to 100, 200, 300 and 400% of its original length for 10 25 seconds, subsequently the fibre is allowed to relax tensionless for 1 hour (room temperature).

The tension set is calculated from:

$$30 \quad \text{Tension set [%]} = \frac{\text{final length} - \text{initial length}}{\text{initial length}} * 100$$

35 Example I

A thermoplastic elastomer was prepared based on a flexible polypropylene homopolymer R xflex FPO D100 of

R xene (containing 53 wt.% amorphous polypropylene as determined by immersion in cyclohexan (of an 0.1 mm film) at roomtemperature), and an EPDM (EPDM-1, being an ethyldene-norbornene (ENB) type EPDM with a M_w (weight average molecular weight) of 6×10^5 (measured by SEC-DV)). The product was prepared in a dynamic vulcanisation process, using a Banbury mixer; SP 1045 (of Schenectady) was used as a phenolic curative. The ingredients used are given in Table I; the results in 10 Table II.

Example II

A TPV was made as per Example I, but instead of Rexflex FPO D100, a flexible polypropylene copolymer, 15 Rexflex FPO D400 (containing 60 wt.% amorphous product) was used. Results are given in Table II.

Comparative experiments A + B

Examples I and II were repeated, but now, instead 20 of the Rexflex polymer, use was made of a polypropylene homo- resp. copolymer resin (PP1 having a meltflow index (determined at 230°C, with 2,16 kg., according to ISO 1133) of 1.2, resp. PP2 having a meltflowindex of 1.0).

25 The results are given in Table II.

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TABLE I

Examples/ Experiments		I-II/A-B
	EPDM (component C)	100
5	Polyolefin (components A+B)	42
	Talc	40
	SP 1045	3.0
	SnCl ₂ . dihydrate	3.0
	ZnO	1.8
10	Phenolic antioxidant	0.9
	Extender oil	164

All ingredients are given in parts per 100 parts of component C.

15

TABLE II

Example/exp.	A	B	I	II	
Hardness (A)	54	45	27	24	
CS@23°C, %	19	17	18	19	
20	M ₁₀₀ , MPa	1.8	1.5	0.7	0.8
	M ₂₀₀ , MPa	2.6	2.3	1.1	1.2
	M ₃₀₀ , MPa	3.2	3.1	1.5	---
	M ₅₀₀ , MPa	4.5	4.4	2.1	---
	TS, MPa	4.7	6.0	2.2	1.5
25	EB, %	530	720	550	280
	ΔH, J/g	11.8	9.7	2.3	1.6
	T _m , °C	148	148	142	136

Example III-VI

Example I was repeated, but as components A and B use was made resp. of PP1 and an amorphous ethylene/propylene copolymer (EP-1, with an M_w of 5 1.9×10^5 , and a crystallinity of 5%) in different ratios. The sum of components A + B is as per Table I. The results are given in Table III.

10

TABLE III

Example	III	IV	V	VI
PP1/EP-1	80/20	60/40	40/60	30/70
Hardness (A)	42	35	30	22
CS @23°C, %	24	18	22	25
CS @70°C, %	32	23	27	35
CS @100°C, %	34	26	32	36
M_{100} , MPa	1.2	0.9	0.8	0.5
M_{200} , MPa	1.9	1.6	1.3	0.8
TS, MPa	2.8	1.8	1.7	1.1
EB, %	410	240	290	290
ΔH , J/g	9.2	6.3	5.2	2.7
T _m , °C	150	150	150	150

25

Example VII

A thermoplastic elastomer was prepared based on a Rexflex FPO D100 of Rexene, and an EPDM (EPDM-2, being an ENB-type EPDM with an M_w of 240,000). The product 30 was prepared in a dynamic vulcanisation process, using a 350 cc Brabender or Banbury mixer. The ingredients used

are given in Table IV.

Subsequently the product was melt-spun to a monofilament elastic fibre, using a Gottfert Viscotester 1500. The results are given in Table V.

5

Example VIII

An elastic monofilament was made as per Example VII, but less Rexflex FPO D100 was used in the preparation of the thermoplastic elastomer. The ingredients are given in Table IV; the results in Table V.

10

Example IX

An elastic monofilament fibre was made as per Example VII, but instead of Rexflex FPO D100, Rexflex FPO 400 was used in the preparation of the thermoplastic elastomer. The ingredients are given in Table IV; the results in Table V.

15

Comparative experiment C

An elastic monofilament fibre was made as per Example VII, but instead of Rexflex FPO D100, use was made of PP1. The ingredients are given in Table IV; the results in Table V.

20

25

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TABLE IV

Examples/exp.	VII	VIII	IX	C
EPDM (component C)	100	100	100	100
Rexflex FPO D100 (component A+B)	70	45	-	-
Rexflex FPO D400 (component A+B)	-	-	70	-
PP1	-	-	-	70
SP 1045	5	5	5	5
SnCl ₂ . dihydrate	1	1	1	1
ZnO	1	1	1	1
Phenolic antioxidant	0.7	0.5	0.7	0.7

15

TABLE V

Examples/exp.	VII	VIII	IX	C
Fineness, tex	105	110	107	132
Tenacity, cN/tex	1.8	1.4	1.7	3.8
Elongation, %	730	680	610	415
Tension set at 100%	5	3	4	5
Tension set at 200%	11	8	10	23
Tension set at 300%	19	17	19	50
Tension set at 400%	33	30	32	215
Tension set at 200%, drawn fibr ¹	3	2	3	-

¹⁾ fibre was drawn up to 400% (for 10 seconds) and relaxed for about 24 hours.

The melt-spun fibres have a low tension set after a large deformation (400%). A decrease in tension set is observed when the fibres are drawn (and relaxed) after the spinning process. Furthermore an increase in 5 tenacity and a small decrease in maximum elongation have been observed.

Examples X-XIV and comparative experiment D

Thermoplastic elastomers were made by dynamic 10 vulcanization in a Brabender Banbury mixer. The ingredients are given in Table VI. Use was made of two homopolymers Rexflex FPO's (D100 and D1720), of two copolymers Rexflex FPO's (D400 and D1820) and, as comparison, use was made of PP1. 15 The rubber (component C) was in all cases EPDM-2.

TABLE VI

Examples	X-XIII	XIV	D
EPDM (C)	100	100	100
Polyolefin (A+B)	70	45	70
SP 1045	5.2	5.2	5.2
SnCl ₂ .dihydrate	0.5	0.5	0.5

25 The results of tension set measurements, after 100%, 200%, 300% and 400% deformation and 1 and 12 hour unstrained relaxation, are given in Table VII.

TABLE VII

Example/ Exp.		Deformation 10 s at	Tension set [%] after 1 hours	Tension set [%] after 12 hours
5	X	Rexflex D100	100%	5
			200%	12
			300%	21
			400%	36
	XI	Rexflex D1720	100%	9
			200%	23
			300%	49
			400%	89
10	XII	Rexflex D400	100%	4
			200%	8
			300%	17
			400%	35
	XIII	Rexflex D1820	100%	8
			200%	21
			300%	46
			400%	83
	XIV	Rexflex D100	100%	3
			200%	8
			300%	17
			400%	33
	D	PP1	100%	14
			200%	57
			300%	128
			400%	215

CLAIMS

1. Thermoplastic elastomer comprising a blend of a rubber and a thermoplastic resin, the rubber being at least partially cured, characterized in that it comprises:
 - A) a thermoplastic resin,
 - B) an amorphous polyolefin, selected from an amorphous α -olefin homopolymer, in which the α -olefin has 3-20 C-atoms, and an amorphous α -olefin copolymer, based on ethylene and a α -olefin having 3-20 C-atoms, and
 - C) an at least partially cured rubber, wherein the ratio of component B to components (A + B) is between 15 and 75 wt.%, the component C is present between 25 and 90 wt.% (based on (A + B + C)), and wherein the amorphous polyolefin (component B) is uncured.
2. Thermoplastic elastomer according to claim 1, characterized in that the thermoplastic resin has a DSC-crystallinity of at least 25%.
3. Thermoplastic elastomer according to anyone of claims 1-2, characterized in that the thermoplastic resin is a thermoplastic olefin resin.
4. Thermoplastic elastomer according to claim 3, characterized in that the thermoplastic olefin resin is selected from homo- or copolymers of polyethylene and polypropylene.
- 30 5. Thermoplastic elastomer according to anyone of claims 1-4, characterized in that the amorphous polyolefin is amorphous polypropylene.
6. Thermoplastic elastomer according to anyone of claims 1-5, characterized in that the amorphous polyolefin has a number average molecular weight M_n of at least 25,000.
- 35 7. Thermoplastic elastomer according to any one of

claims 1-6, characterized in that the rubber is selected from the group of EADM and butylrubber.

8. Thermoplastic elastomer according to anyone of claims 1-7, characterized in that the ratio of amorphous polyolefin to (thermoplastic resin + amorphous polyolefin) is 20-70 wt.%.

5 9. Thermoplastic elastomer according to anyone of claims 1-8, characterized in that a flexible polyolefine is used for the combination of components (A + B).

10 10. Thermoplastic elastomer according to anyone of claims 1-9, characterized in that the rubber is cured to the extend that not more than 15% of the rubber is extractable.

15 11. Thermoplastic elastomer according to claim 10, characterized in that not more than 5% of the rubber is extractable.

12. Thermoplastic elastomer according to anyone of claims 1-11, characterized in that the amount of component A is between 10-25 wt.% per 100 parts of components (A + B + C).

20 25 13. Process for the preparation of a thermoplastic elastomer according to anyone of claims 1-12 characterized in that the thermoplastic elastomer is prepared by mixing the components and subjecting the blend to a dynamic curing process.

14. Process according to claim 13, characterized in that components A + B are premixed, before they are blended with the other ingredients.

30 15. Process according to claim 13, characterized in that component B is added after the completed cure of component C.

16. Elastomeric fiber comprising a thermoplastic elastomer according to anyone of claim 1-12.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 97/00136

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L23/16 C08L23/10 C08L101/00 D01F6/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08L D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 320 001 A (HIMONT INC) 14 June 1989 see claims ---	1-15
X	EP 0 452 089 A (SUMITOMO CHEMICAL CO) 16 October 1991 see page 2, paragraph 1 see page 4, line 18 - line 34 see page 5, line 45 - page 6, line 5; claims ---	1-15
X	EP 0 634 453 A (MITSUI PETROCHEMICAL IND) 18 January 1995 see page 10, line 15 - line 30; claims 1-4 ---	1-15

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
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- 'O' document referring to an oral disclosure, use, exhibition or other means
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- 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

6 June 1997

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 97/00136

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 017, no. 567 (C-1120), 14 October 1993 & JP 05 163396 A (TONEN CHEM CORP), 29 June 1993, see abstract & DATABASE WPI Derwent Publications Ltd., London, GB; AN 93-240113 see abstract -----</p>	16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 97/00136

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EP 0634453 A	18-01-95	JP 7060907 A JP 7096581 A JP 7070380 A CA 2127575 A US 5596042 A	07-03-95 11-04-95 14-03-95 09-01-95 21-01-97